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ab-Initio Molecular Dynamics Simulations of Molten Ni-Based Superalloys

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Abstract

In the casting of single-crystal turbine blades, the composition (c) and temperature (T) dependencies of the liquid-phase molar volume (V(c,T)) play a critical role in driving convective instabilities and the associated formation of solidification defects. To support an effort aimed at the development of validated mathematical criteria for predicting solidification defect formation in Ni-based superalloys, ab-initio molecular dynamics (AIMD) simulations have been performed for elemental, binary and ternary alloys of Ni with Al, W, and Re, to compute equations of state at temperatures of 1,830K and 1,750K. Where comparisons with measurements are available, AIMD-calculated volumes agree to within 0.5–2.5% of experiment. The results are used to test the accuracy of the predictions of a recently proposed parametrization for composition and temperature dependent molar volumes in liquid multicomponent superalloys. For Ni-Re the model is found to be highly accurate over a wide range of compositions while for Ni-W it gives rise to qualitatively incorrect predictions at higher W concentrations.

1. Introduction

In the casting of single-crystal turbine blades for high-performance jet engines, the formation of solidification defects has become an increasingly important problem due to the rising levels of refractory elements in commercial Ni-based superalloys. While refractory elements have the desirable effect of improving high-temperature creep strength, they also enhance density-driven convective instabilities underlying the formation of so-called freckle defects (chains of small equiaxed grains) in directional solidification. The high-angle grain boundaries and composition gradients associated with freckles adversely affect mechanical properties, and the optimization of superalloys for high-performance applications requires a quantitative model for predicting refractory metal compositions that will allow commercial castings that avoid these defects.

Freckles develop due to thermo-solutal convection in the molten alloy during solidification, and it has been suggested that they will form when a critical Rayleigh number is exceeded[1-4]. The Rayleigh number (R) is a measure of the ratio of the buoyancy force to the retarding frictional force in the mushy zone:

$$R = \left(\Delta\rho/\overline{\rho}\right)gKl / \alpha v \tag{1}$$

where l is an appropriate length scale, K is the average permeability, g gravitational acceleration, α is the thermal diffusivity, v is the kinematic viscosity of the fluid, and $\left(\Delta\rho/\overline{\rho}\right)$, the density contrast, is a measure of the density variation over the mushy zone between the solid and liquid phases. The tendency towards defect formation is highly sensitive to the primary dendrite arm spacing (which determines the permeability), as well as the density contrast. An open question concerning the predictive power of the Rayleigh-number criterion for freckle formation is the fact that it assumes the density gradients are aligned with gravity. This is not the case in most castings since heat losses through the mold create horizontal thermal gradients and hence tilted solid-liquid interfaces. The work presented in this paper is a component of a multi-institutional effort, supported

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through the Air Force Office of Scientific Research Materials Engineering for Affordable New Systems (AFOSR-MEANS) program, aimed at the development of validated mathematical criteria for predicting solidification-defect formation in the casting of single-crystal Ni-based superalloys. A model ternary Ni-Al-W superalloy system has been chosen as an initial focus of the experimental and modeling efforts to validate the physical models.

To validate mathematical models for freckle formation in specific alloy systems, it is that the values of the various parameters in Eq. (1) are accurately known. Determination of the permeability and density gradients poses a major challenge in this regard. In the MEANS project, values for the permeability are being derived from fluid-flow simulations employing realistic models for the mushy-zone topology obtained from three-dimensional reconstructions derived by serial sectioning.[5] The focus of the work presented here, performed with high performance computing (HPC) Challenge support, is the application of AIMD simulations as a computational framework for aiding the development and validation of accurate models for $\Delta\rho$. In directional solidification, $\Delta\rho$ represents the mass-density difference between the hot liquid near the dendritic solid-liquid interface and the cooler melt at the top and side-walls of the casting. The density contrast is therefore related both to the temperature gradients present during casting, as well as the variations in solute concentration in the melt that develop as a consequence of equilibrium partitioning between solid and liquid phases. The mass-density difference thus originates from both the composition (c) and temperature (T) dependencies of the liquid-phase molar volume $V(c,T)$.

Very recently, Mukai, et al.[6–9], performed detailed measurements of the densities of several binary liquid Ni-based alloys, and a few representative ternaries, as functions of c and T. The results of their measurements have been used to develop a thorough parameterization for $V(c,T)$ in superalloys[8]. Due to the lack of extensive data for multicomponent systems, a key assumption made in developing the parameterization is that the partial-molar volume of each solute species is independent of the compositions of the others. The effects upon $V(c,T)$ arising from the interactions between solute atoms of different types are thus neglected. Further, measured density data for some key elements such as Re are unavailable and the partial molar volumes for these elements are treated as parameters to fit available data for multicomponent superalloys. Comparisons between the predictions of the Mukai parameterization and available data for densities of commercial superalloys show agreement at the level of a few percent. At present, experimental data for ternary Ni-Al-W alloys is not available, and estimates of the accuracy of the Mukai

model for liquid density in this system, which forms the focus of our MEANS project, are thus not readily obtained. The work presented here makes use of state-of-the-art AIMD simulations as a means for testing the accuracy of the model for parametrizing $\rho(c, T)$ in this system. These calculations are also being used to independently test the accuracy of the Mukai parameters for elements where direct measurements of liquid density are unavailable.

2. Method

The properties of molten Ni-based alloys have been computed within the framework of AIMD simulations. In these simulations, ionic positions were evolved in time employing classical Nosé-Hoover dynamics (fixed particle number, volume, and temperature MD)[9,10] using interatomic forces computed directly within the framework of electronic density functional theory (DFT). The current implementation of AIMD makes use of the commercial DFT software VASP (Vienna *ab-initio* simulation package)[11–13], developed at the Institut für Materialphysik of the Univerität Wien. The VASP code scales well for systems with large numbers of atoms on parallel computers with high-bandwidth communications networks. The computational problem involves repeated applications of fast-fourier-transform and iterative diagonalization algorithms. While the problem is far from embarrassingly parallel overall, nearly linear scaling is achieved for representative calculations up to approximately 128 processors for AIMD runs performed on an SGI O3K and Altix, as we have documented previously[14]. The underlying algorithms employed in VASP have been extensively tested and optimized for parallel processing with large numbers of processors. The production runs performed in this work each involved the use of 64 processors.

In the liquid-alloy simulations we employed 500-atom cubic supercells and periodic boundary conditions with fixed periodic lengths. Below we present results obtained to date for seven alloy compositions, which are referred to in terms of the number of each type of atom in the simulation cell: Ni_{500}, $Ni_{400}Al_{100}$, $Ni_{473}W_{27}$, $Ni_{400}W_{100}$, $Ni_{473}Re_{27}$, $Ni_{400}Re_{100}$, and $Ni_{436}Al_{50}W_{14}$. Consistent with the goals summarized in the previous section, the alloy compositions are chosen to test the accuracy of the available parameterization[8] for $V(c,T)$ in its application to the ternary Ni-Al-W alloys being considered for the validation experiments within our MEANS program, and for important superalloy refractory additions such as Re, for which experimentally measured data is currently unavailable.

The details of the calculations are as described by us previously[14] and are only briefly summarized here.

Nosé-Hoover equations of motion were integrated specifying thermostat temperatures of T=1,830K and T=1,750K. The time steps (Δt) for the molecular dynamics (MD) simulations were chosen as Δt=0.002 ps or Δt=0.003 ps, to ensure that the conserved energy in the Nosé-Hoover dynamics displayed a drift in time no larger than 1 meV/atom ps. The starting configuration for the Ni_{500} and $Ni_{400}Al_{100}$ simulations were obtained from snapshots derived from classical molecular-dynamics simulations based on classical interatomic potentials[15], for the Ni-W, Ni-Re, and Ni-Al-W simulations the initial configurations were obtained by replacing Ni and Al atoms, selected at random, by W and Re. At each MD time step the self-consistent charge density and associated interatomic forces were computed for integration of the ionic trajectories, and relevant system properties including the pressure, energy, temperature and atomic coordinates were stored. The DFT calculations made use of ultrasoft pseudopotentials[16,17] and the PW91 generalized-gradient approximation (GGA)[18]. The electronic wavefunctions were represented in a plane-wave basis set with a cutoff energy of 260 eV. The simulations employ a single k-point (Γ) in performing reciprocal-space summations, with electronic eigenvalues occupied according to Fermi statistics with an electronic temperature equal to that for the ions. For each alloy composition, simulations were performed over a range of volumes spanning plus or minus five percent of the experimentally measured or estimated equilibrium value. Total simulation times ranged from 5–10 ps, a time interval long enough to obtain good statistical precision in calculated equation-of-state parameters[14]. As described below, the system size and simulation time were sufficient to observe appreciable solute diffusion and realistic liquid structures.

3. Results and Analysis

The main focus of the AIMD simulations is the calculation of molar volumes for representative binary and ternary alloy compositions in Ni-based superalloys. In calculations of such equilibrium properties for a liquid alloy, it is important to establish that (i) the simulations are run sufficiently long in time to observe appreciable solute interdiffusion, and (ii) that the periodic system size is large enough to give a realistic liquid structure. If the runs are performed for too short a period, the calculated thermal averages may be biased by the choice of the initial atomic configurations. Further, if the system is too small the positional correlations may not decay sufficiently over the length of the simulation box, giving rise to an artificially enhanced degree of order in the simulated melt structures.

Considering first point (i), Figure 1 plots averaged mean-square displacements for Ni, W, Al, and Re, as calculated from the T=1,830K simulations for the pure-Ni melt, and for each of the binary $Ni_{400}X_{100}$ samples (X=Al, W, and Re). The slopes of the best-fit lines relating mean-square displacements and time are used to derive the estimates of the concentration-dependent tracer-diffusion constants listed in the panels. A comparison of the results indicates that Re and W are the slowest diffusing elements in these alloys, as expected, based on their large sizes and heavy atomic masses. It is also interesting to note that the Ni diffusion constant is lower in the Ni-X melts, relative to pure Ni, despite the fact that the average atomic volume is larger in the alloys. This result is consistent with relatively strong solute-solvent interactions in the alloy melts (see below). From the standpoint of the accuracy of the calculations, it is important to note that Figure 1 establishes that significant interdiffusion is occurring over the timescale of the AIMD simulations. Thus, it is expected that the runs are performed over sufficiently long times to give robust estimates of the equilibrium molar volumes. This expectation is supported by the relatively small estimated statistical uncertainties in this property quoted below. It is further supported by the results of a test performed for binary Ni-W samples, whereby two different initial atomic configurations were used to compute the equilibrium volume and the final results were found to agree within statistical uncertainties.

Figure 2 plots calculated radial distribution functions $g_{\alpha-\beta}$ (r) for each of the (α,β) pairs of species in pure Ni and binary $Ni_{400}X_{100}$ (X=Al, W, and Re) melts. Considering point (ii) above, it is noteworthy that each of these distribution functions converges to the uncorrelated limit of unity over a distance less than half the periodic dimensions of our simulation cells. The results in Figure 2 also give insight into the nature of the chemical ordering in the alloy melts. Specifically, the larger value of the main peak g_{Ni-X}, relative to those for the solute-solute (X-X) and solvent-solvent (Ni-Ni) pairs, is indicative of a preference for neighbors between unlike species, i.e., for chemical short-range ordering. Similarly, it is noteworthy that the average nearest-neighbor bond length for Ni-X pairs (approximately 2.485 $\mathring{A}$) is significantly smaller than the average of the Ni-Ni and X-X bond lengths (roughly 2.59 $\mathring{A}$). Both results are indicative of a significant preference for chemical short-range ordering between Ni and X species in each of the systems considered.

To compute equilibrium values of V, AIMD simulations were performed for a series of volumes at each composition and the average pressure (P) was calculated as the basis for fitting the equation of state. As described previously[14], for each simulation at a given volume the results show that after an initial short

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transient, lasting a few tenths of a ps, the pressure displays equilibrium fluctuations about a well defined average value. An analysis of the time scale and amplitude of these equilibrium fluctuations is used to derive estimates of the statistical uncertainties in the calculated time-averaged pressure. For each temperature and composition a total of three to four volumes were considered. The calculated time-averaged pressures were then used to derive an equation of state, assuming a quadratic relationship between P and V. From the fitted equation of state we computed the equilibrium (zero-pressure) volume (V), as well as the bulk modulus and its pressure derivative[14]. Finally, statistical uncertainties were estimated based on the error estimates for each of the individual average pressures. The results are recorded in Table 1, listing calculated equilibrium volumes for each of the seven liquid Ni-based alloy compositions considered to date. Data for all compositions at T=1,830K are included, and initial results for two compositions are also included at T=1,750K.

Table 1. Calculated atomic volumes for molten Ni-based alloys at T=1,830K and T=1,750K. The numbers in parentheses represent estimated 95% confidence intervals on the last digit. The calculated AIMD results are compared with the predictions of the parametrized model due to Mukai, et al.[8]

Composition	V(T=1750 K) (cm³/mole)		V(T=1830 K) (cm³/mole)	
	AIMD	Mukai	AIMD	Mukai
Ni$_{500}$	7.64(1)	7.4597	7.71(1)	7.5727
Ni$_{400}$Al$_{100}$		7.7628	7.94(1)	7.8525
Ni$_{400}$W$_{100}$	8.01(1)	6.5192	8.05(1)	7.3598
Ni$_{473}$W$_{27}$		7.5534	7.70(1)	7.6557
Ni$_{400}$Re$_{100}$		7.5869	7.98(1)	7.8695
Ni$_{473}$Re$_{27}$		7.4940	7.76(1)	7.6557
Ni$_{436}$Al$_{50}$W$_{14}$		7.6920	7.81(1)	7.7682

In Table 1, values from the most recent parametrization of molten superalloy densities, due to Mukai, et al.[9] are listed along side the AIMD results for each of the alloy compositions considered. For elemental Ni, and the binary Ni-Al and Ni-W systems, the Mukai model reproduces well the directly measured densities obtained at these same compositions and temperatures[6,7]. Thus, for the Ni$_{500}$, Ni$_{400}$Al$_{100}$, and Ni$_{473}$W$_{27}$ systems, a comparison between the Mukai and AIMD results can be considered as representing a direct comparison between experimental measurements and calculations. The largest discrepancy is found for elemental Ni, where the agreement between measured and calculated values of V is still very good, at the level of 1.8% at T=1,830K, and 2.4% at T=1,750K. For Ni-Al and Ni-W, the agreement between experiment and theory is slightly better, 1.1% and 0.6%, respectively. For each of these systems the calculated molar volumes are larger than the

measurements, a trend that is often found for solid-state *ab-initio* calculations performed within the generalized-gradient approximation to DFT. As a result of the comparisons between experiment and theory for Ni, Ni-Al and Ni-W systems, it is reasonable to conclude that the GGA introduces a positive systematic error in the prediction of the Ni-based liquid atomic volumes, on the order of 0.5–2.5% for the alloy compositions and temperatures considered.

As described in the Introduction, the primary motivation for the present work is to use AIMD simulations as a framework for developing and validating predictive models for $\rho(c, T)$ in Ni-based superalloys. For this purpose, we consider further the most current parametrization for $V(c, T)$ proposed by Mukai, et al.[8]. We consider cases where there is no experimental data available, and use the AIMD results as a basis for testing the accuracy of the Mukai model in predictions for compositions where it has not been fit. We consider first a ternary Ni-Al-W melt representative of the compositions that are being considered in the experimental effort within our MEANS program. The alloy Ni$_{436}$Al$_{50}$W$_{14}$ listed in Table 1 has a composition which represents an average of those for the binary Ni$_{400}$Al$_{100}$ and Ni$_{473}$W$_{27}$ melts that is also considered in this work. Both the AIMD and Mukai results predict that the volume of the ternary alloy is well approximated (to within 0.2%) by a linear interpolation between the binary alloy values. This result suggests that one of the main assumptions in the Mukai parametrization, namely that the partial molar volumes of the binary alloys can be used to interpolate molar volumes for multicomponent systems, is reasonably accurate in the Ni-Al-W system.

A second test of the Mukai model is made based on the results plotted in the right panel of Figure 3, corresponding to composition dependent molar volumes for Ni-Re alloys. In this binary system no measured data is available for liquid volumes, and the partial molar volume of Re was obtained as a fitting parameter by Mukai, et al., to reproduce data from a multicomponent superalloy system. The comparisons between the AIMD and Mukai results for Ni-Re are seen to be in very good agreement: both sets of results show a highly linear dependence of V on Re concentration. From the slope of the fitted lines in Figure 3 the partial molar volume of Re $\overline{V}_{Re}$ in molten Ni can be extracted. The AIMD simulations and Mukai model are in very good agreement, predicting values for V Re that are approximately 20% larger than the molar volume of molten Ni at T=1,830K (see insets in Figure 3). While the comparison between AIMD and the Mukai model is thus very favorable for Ni-Re, stong discrepancies are found for the Ni-W system, as indicated by the results in the left panel of Figure 3. For Ni-W both the Mukai model and the AIMD calculations

predict strongly non-linear dependencies of V on composition, but qualitatively different trends are found for the nature of this non-linearity. Specifically, the Mukai model predicts that the addition of high concentrations of W gives rise to a *decrease* in the volume of molten Ni-W alloys relative to pure Ni, in sharp contrast with the AIMD calculations. The slopes of the fitted volume versus concentration relations in the pure-Ni limit can be used to derive the partial molar volume for W in Ni at infinite dilution $\overline{V}_W^\infty$, and for this quantity relatively large discrepancies are seen again between the AIMD values and the predictions of the Mukai model. The AIMD results thus call into question the accuracy of the Mukai parametrization for concentrated Ni-W melts, and suggest that the reliability of this parameterization for superalloys containing W is limited to the range of dilute W compositions where it was fit.

4. Summary

AIMD simulations have been performed to derive liquid-phase atomic volumes for seven elemental, binary and ternary alloy compositions of molten Ni with Al, W, and Re additions to compute atomic volumes at temperatures of 1,830K and 1,750K. Comparisons between AIMD results and direct measurements for Ni, Ni-Al, and Ni-W, yield agreement at the level of 0.5–2.5%, with the calculated volumes being systematically larger than experimental volumes. Simulations were performed for a ternary Ni-Al-W composition where the accuracy of the most recent parametrization for molten superalloy densities was affirmed. The results also support the accuracy of the parametrization for Ni-Re, but suggest that its reliability for superalloys containing W is limited to the range of dilute W compositions where it was fit to experimental data. Future work will involve further AIMD calculations to more thoroughly test, and refine as necessary, the accuracy of the current published parametrization for $V(c,T)$ over the range of compositions and temperature relevant for superalloy solidification. This will include calculations for Ni-Ta, as well as ternary Ni-Al-Re and Ni-Al-Ta alloys to test (i) the reliability of the main assumptions underlying the published parametrization, related to the interpolation of multicomponent volumes from binary data, and (ii) the origin of the anamolously large temperature dependencies found in the parametrized values of the partial molar volumes for the refractory elements W, Ta, and Re[8]. Future calculations will benefit from the completion, over the past fiscal year, of an extensive effort leading to the implementation of fixed-pressure dynamics into the VASP code[19]. These advances should allow calculation of equilibrium atomic volumes in about one-third the time required by fitting equations of state to fixed-volume simulation data. Further, we will explore statistical reweighting techniques to evaluate pressure (or volume) responses arising from dilute solute additions to molten Ni-based superalloys.

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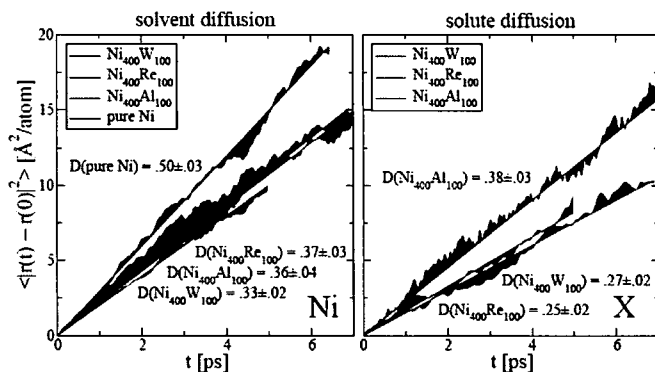19. Lill, J., D.R. Trinkle, and C. Woodward, unpublished work, 2007.

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Figure 1. Calculated mean-square displacements versus simulation time derived from AIMD simulations for elemental Ni and binary Ni-X (X=Al, W, and Re) alloys at T=1,830K. The filled areas show the deviation in the "random walk" from the long-time linear diffusion relation $\langle |r(t) - r(0)|^2 \rangle = 6Dt$ for each species. Estimates of the self-diffusion constants D, reported in units of $\text{Å}^2/\text{ps}$ ($10^{-4}\text{cm}^2/\text{s}$), are indicated in each of the panels.

Figure 3. Molar volumes versus concentration in binary Ni-W and Ni-Re melts at T=1,833K. The solid blue and red circles represent results from AIMD simulations and the parametrization due to Mukai, et al.[8], respectively. The solid lines represent best fits to the data, assuming a quadratic and linear dependencies of volume on concentration for Ni-W and Ni-Re, respectively. The insets in each panel give calculated ratios between the partial molar volumes of the solutes (at infinite dilution) and the molar volume of the pure Ni melt.
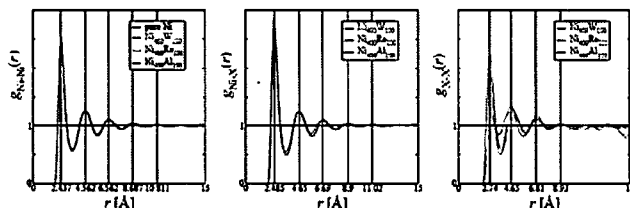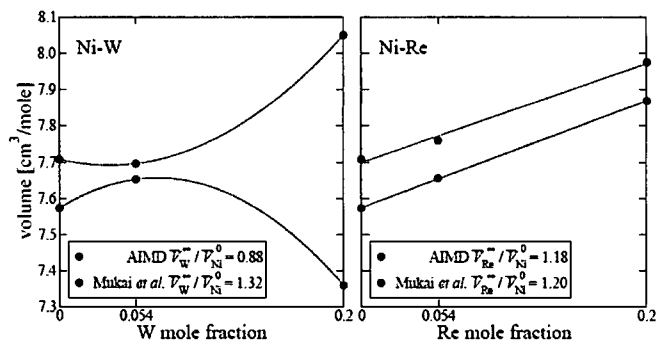

Figure 2. Calculated radial distribution functions derived from AIMD simulations for elemental Ni and binary Ni-X (X=Al, W and Re) alloys at T=1,830K. Results are plotted solvent-solvent (Ni-Ni), solute-solvent (Ni-X) and solvent-solvent (X-X) pairs.